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Onsager's reciprocal relations for non linear systems

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1. Non equilibrium thermodynamics in its conventional form[1] is characterized by the linearity of the phenomenological relations between fluxes $\frac{d\alpha^{\mu}}{dt}$ and affinities ξ_{μ}

$$\frac{d\alpha^{\mu}}{dt} = L^{\mu\nu}\xi_{\nu} \qquad (\mu, \nu = 1, \ldots, n, \text{ summation convention}). \tag{1}$$

Further the connection between thermodynamic coordinates α^{μ} and affinities is linear

$$\xi_{\mu} = -s_{\mu\nu}\alpha^{\nu} \left(s_{\mu\nu} = -\frac{\partial^2 S}{\partial\alpha^{\mu}\partial\alpha^{\nu}}(\alpha = 0),\ S(\alpha) = \text{entropy function}\right). \tag{2}$$

The time reversal invariance of the fundamental mechanical equations of motion is reflected by Onsager's reciprocal relations for the phenomenological coefficients $L^{\mu\nu}$

$$T^{\mu}_{\mu'} T^{\nu}_{\nu'} L^{\mu'\nu'} = L^{\nu\mu} \quad (T^{\mu}_{\mu'} T^{\mu'}_{\nu} = \delta^{\mu}_{\nu}), \tag{3}$$

where T^{μ}_{ν} is the representative of the time reversal operation, that is with a suitable choice of coordinate system

$$T^{\mu}_{\nu} = 0\ (\mu \neq \nu), \qquad T^{\mu}_{\mu} = \begin{matrix} +1 & (\alpha^{\mu}\text{ even}) \\ -1 & (\alpha^{\mu}\text{ odd}) \end{matrix}. \tag{4}$$

Sometimes the linear approximation (1), (2) is invalid and in the phenomenological equations

$$\frac{d\alpha^{\mu}}{dt} = a^{\mu}(\alpha) \tag{5}$$

the functions $a^{\mu}(\alpha)$ are not linear. It is natural to ask whether in the case (5) of non linear relaxation the time reversal invariance of the mechanical equations of motion will give rise to generalized reciprocal relations which reduce to

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[1] E.g. [de Groot, 1951].

Onsager's relations in the linear case. In this note we shall show that as a consequence of the time reversal invariance the equation (5) can be written

$$\frac{d\alpha^\mu}{dt} = f(\alpha)^{-1}\frac{\partial}{\partial\alpha^\nu}[L^{\mu\nu}(\alpha) f(\alpha)] = L^{\mu\nu}(\alpha)\frac{\partial \log f(\alpha)}{\partial\alpha^\nu} + \frac{\partial L^{\mu\nu}(\alpha)}{\partial\alpha^\nu}, \tag{6}$$

where $f(\alpha)$ is the density of the thermodynamic equilibrium distribution of the α-observables and $L^{\mu\nu}(\alpha)$ satisfies

$$T^\mu_{\mu'} T^\nu_{\nu'} L^{\mu'\nu'}(T\alpha) = L^{\nu\mu}(\alpha), \tag{7}$$

where T^μ_ν has the same meaning as above. The equilibrium distribution is invariant under time reversal and as the Jacobian $\left|\frac{\partial(T\alpha)}{\partial(\alpha)}\right| = 1$, we obtain

$$f(T\alpha) = f(\alpha). \tag{8}$$

If in particular $L^{\mu\nu}(\alpha)$ is independent of α and if $f(\alpha)$ has the Gaussian form

$$f(\alpha) \sim \exp\{-\tfrac{1}{2} s_{\mu\nu}\alpha^\mu\alpha^\nu\}^1 \tag{9}$$

it is seen that (6) is identical with (2), and (7) with (3).

2. The proof of (6) belongs to statistical mechanics. We have associated with the α-observables an equilibrium distribution—not necessarily a probability distribution—

$$f(\alpha)\,d\alpha \tag{10}$$

in the n-dimensional real space of the thermodynamic coordinates. The temporal change of the α-observables is partly characterized by the transition probability distribution

$$P(s,\alpha;t,I). \tag{11}$$

The expression (11) represents the probability of finding at the time t a value of the observable in the n-dimensional interval I, if at the previous time s the value of the observable is known to be the n-dimensional point α.

The transition probability distribution (11) is assumed to have the following properties (on a macroscopic time scale).

a. For fixed real values $s, t\ (s \leq t)$ and fixed α in the n-dimensional real space R^n, $P(s,\alpha;t,.)$ determines a probability distribution in R^n.

b. For fixed s, t, and I the derivatives

$$\frac{\partial}{\partial\alpha^\mu} P(s,\alpha;t,I) \quad\text{and}\quad \frac{\partial^2}{\partial\alpha^\mu\partial\alpha^\nu} P(s,\alpha;t,I) \tag{12}$$

exist as continuous functions of α.

c. Continuity condition. For arbitrary $\delta > 0$

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[1] Boltzmann's constant = 1.

$$\lim_{(t-s)\downarrow 0} \frac{1}{t-s} \int\limits_{|\alpha'-\alpha|>\delta} P(s,\alpha;t,d\alpha') = 0.^{1} \tag{13}$$

It follows from this assumption that

$$\lim_{(t-s)\downarrow 0} P(s,\alpha;t,I) = \begin{matrix} 1 & (\alpha\in I) \\ 0 & (\alpha\notin I) \end{matrix}. \tag{14}$$

d. Kolmogorov's conditions.[2] For arbitrary $\delta>0$ the following limits exist

$$\lim_{(t-s)\downarrow 0} \frac{1}{t-s} \int\limits_{|\alpha'-\alpha|\leqslant\delta} P(s,\alpha;t,d\alpha')(\alpha'^{\mu}-\alpha^{\mu}) = a^{\mu}(\alpha,t), \tag{15}$$

$$\lim_{(t-s)\downarrow 0} \frac{1}{t-s} \int\limits_{|\alpha'-\alpha|\leqslant\delta} P(s,\alpha;t,d\alpha')(\alpha'^{\mu}-\alpha^{\mu})(\alpha'^{\nu}-\alpha^{\nu}) = b^{\mu\nu}(\alpha,t). \tag{16}$$

It follows from the continuity condition *c.* that the limits $a^{\mu}(\alpha,t)$ and $b^{\mu\nu}(\alpha,t)$ are in fact independent of δ. Further it follows that for arbitrary real numbers $k_1,\ldots,k_n$ the expression

$$b^{\mu\nu}(\alpha,t)\,k_{\mu}k_{\nu} \tag{17}$$

is non negative.

Let $\varphi(.)$ be an arbitrary complex function on R^n, continuous and bounded and having continuous derivatives $\dfrac{\partial\varphi(\alpha)}{\partial\alpha^{\mu}}$ and $\dfrac{\partial^2\varphi(\alpha)}{\partial\alpha^{\mu}\partial\alpha^{\nu}}$. The conditioning transformation $C(s,t)$ is defined by

$$C(s,t)\varphi(\alpha) \equiv \int\limits_{R^n} P(s,\alpha;t,d\alpha')\varphi(\alpha'), \tag{18}$$

and represents the conditional expectation of the function $\varphi(.)$ of the observable at the time t given the value α of the observable at the time s. Evidently the transform $C(s,t)\varphi$ of φ is according to the assumption *b* above bounded and twice continuously differentiable.

It follows by standard methods[2] from the continuity condition and from Kolmogorov's conditions that the limit

$$\begin{aligned}\left[\frac{\partial}{\partial t} C(s,t)\varphi(x)\right]_{s=t} &= \lim_{(t-s)\downarrow 0} \frac{C(s,t)-1}{t-s}\varphi(\alpha) = \\ &= \lim_{(t-s)\downarrow 0} \frac{1}{t-s} \int\limits_{R^n} P(s,\alpha;t,d\alpha')[\varphi(\alpha')-\varphi(\alpha)]\end{aligned} \tag{19}$$

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[1] $|\alpha|^2 = \sum_{\mu=1}^{\mu=n} |\alpha^{\mu}|^2$.

[2] E.g. [Gnedenko, 1958]. Kolmogorov's conditions are usually associated with Markov processes of the s.c. continuous type. Here, however we are not assuming that the transition probability distribution (11) can correspond to a Markov process.

exists and is equal to

$$M(t)\,\varphi(\alpha) = a^{\mu}(\alpha, t)\frac{\partial \varphi(\alpha)}{\partial \alpha^{\mu}} + \tfrac{1}{2}\, b^{\mu\nu}(\alpha, t)\,\frac{\partial^2 \varphi(\alpha)}{\partial \alpha^{\mu}\,\partial \alpha^{\nu}}, \tag{20}$$

or in operator form

$$\lim_{(t-s)\downarrow 0} \frac{C(s,t) - 1}{t - s} = M(t)\,. \tag{21}$$

In the following we shall call $M(t)$ the *transport operator* corresponding to the α-observables.

e. We may restrict ourselves to the temporally homogeneous case so that the transition probability distribution $P(s, \alpha; t, I)$ is a function only of the time difference $(t - s)$

$$P(s, \alpha; t, I) = P(\alpha; t - s, I), \tag{22}$$

or equivalently

$$C(s, t) = C(t - s). \tag{23}$$

In this case the transport operator $M(.)$ is independent of the time

$$M(t) = M. \tag{24}$$

The following transformation property of the transport operator M is sometimes useful. Let

$$u^1 = u^1(\alpha), \ldots, u^m = u^m(\alpha) \tag{25}$$

be m functions of the n-dimensional variable α, having continuous partial derivatives of the second order. Applying the transport operator M to the function

$$\varphi(\alpha) = \psi(u^1(\alpha), \ldots, u^m(\alpha)) \tag{26}$$

we obtain directly by formal calculations

$$M\varphi = (M u^j)\frac{\partial \psi}{\partial u^j} + b^{\mu\nu}\frac{\partial u^j\,\partial u^k}{\partial \alpha^{\mu}\,\partial \alpha^{\nu}}\,\frac{\partial^2 \psi}{\partial u^j\,\partial u^k}\,. \tag{27}$$

3. We have assumed that the distribution (10) corresponds to equilibrium. This implies that the transition probability distribution (11) admits the distribution (10) as a stationary distribution, that is

$$\int_{R^n} f(\alpha)\,d\alpha\,P(\alpha; t, I) = \int_I f(\alpha)\,d\alpha\,. \tag{28}$$

Hence for an "arbitrary" function $\varphi(\alpha)$

$$\int_{R^n} M\varphi(\alpha)\,f(\alpha)\,d\alpha = 0\,. \tag{29}$$

By formal partial integration we find that (29) is equivalent to

$$\frac{\partial}{\partial \alpha^{\mu}}\left[a^{\mu}(\alpha) f(\alpha)-\frac{1}{2} \frac{\partial}{\partial \alpha^{\nu}} b^{\mu \nu}(\alpha) f(\alpha)\right]=0 . \tag{30}$$

It is seen at once from (30) that the expression

$$J^{\mu}(\alpha)=a^{\mu}(\alpha) f(\alpha)-\frac{1}{2} \frac{\partial}{\partial \alpha^{\nu}} b^{\mu \nu}(\alpha) f(\alpha) \tag{31}$$

may be heuristically considered as the component of a flow vector in the n-dimensional real space. The relation (30) then expresses the fact that the flow is incompressible (divergence free). The incompressibility relation (30) is obviously satisfied automatically if we make the generally much stronger assumption of *detailed equilibrium*

$$J^{\mu}(\alpha) \equiv 0. \tag{32}$$

It follows from (31) that in the case of *detailed equilibrium* the coefficient $a^{\mu}(\alpha)$ is determined by $f(\alpha)$ and $b^{\mu\nu}(\alpha)$

$$a^{\mu}(\alpha)=f(\alpha)^{-1} \frac{\partial}{\partial \alpha^{\nu}}\left(\tfrac{1}{2} b^{\mu \nu}(\alpha) f(\alpha)\right) . \tag{33}$$

This relation is indeed of the form (5), (6). We shall see that this relation can really be derived from statistical mechanics. It may be noticed however that in the one-dimensional case ($n=1$) detailed equilibrium holds already if, as is frequently the case in the applications

$$\int_{-\infty}^{+\infty} f(\alpha)|a(\alpha)| d \alpha<\infty, \quad \lim_{|\alpha| \rightarrow \infty} f(\alpha) b(\alpha)=0 . \tag{34}$$

For, integrating (30) we find

$$a(\alpha) f(\alpha)-\frac{1}{2} \frac{d}{d \alpha} f(\alpha) b(\alpha)=\text{const.} \tag{35}$$

Integrating both sides of the equation over an unbounded interval we obtain on the left a finite value whereas on the right we obtain a finite value if and only if the constant is chosen to be zero. Hence (32) must be satisfied.

4. For the further study of the transport operator M it is convenient to introduce the Hilbert space L^2 of complex functions of the n-dimensional real variable $\alpha, X(\alpha), Y(\alpha), \ldots$ square integrable with respect to the measure $f(\alpha)\,d\alpha$. The scalar product in L^2 is defined by

$$\langle X \mid Y\rangle=\int_{R^{n}} \overline{X(\alpha)}\, Y(\alpha) f(\alpha)\, d \alpha \tag{36}$$

and the norm of an element X of L^2 by

$$\| X \| = \langle X \mid X \rangle^{1/2}. \tag{37}$$

From the invariance of $f(\alpha)\, d\alpha$, (28) it follows at once by application of Schwarz' inequality that the conditioning operator $C(t)$ is bounded by one

$$\| C(t) X \| \leqslant \| X \|. \tag{38}$$

As a consequence of the invariance (8) the time reversal transformation T in L^2 defined by

$$T X(\alpha) = X(T\alpha) \tag{39}$$

is a unitary involution

$$T = T^* = T^{-1}, \tag{40}$$

the * denoting Hermitian adjoint.

The time reversal invariance of the mechanical equations of motion gives rise to the symmetry

$$\int_{I_s} f(\alpha)\, d\alpha\, P(\alpha; t, I_t) = \int_{TI_t} f(\alpha)\, d\alpha\, P(\alpha; t, T I_s) \tag{41}$$

for arbitrary n-dimensional intervals I_s, I_t; TI denoting the "time reversed interval". In terms of the time reversal transformation (39) and the conditioning operator $C(t)$ the relation (41) can be expressed as

$$T C(t) T = C(-t) = C(t)^*. \tag{42}$$

Hence we find that the transport operator M satisfies

$$T M T = M^*. \tag{43}$$

The relation (43) is symbolic as the operator M, being unbounded, is not defined in the whole of L^2. Howewer its domain of definition is dense in L^2.

We now procede to determine M^*. By the definition and using (27)

$$\langle X \mid M^* Y \rangle = \langle M X \mid Y \rangle = \int_{R^n} (M \bar{X})\, Y f\, d\alpha =$$

$$= \int_{R^n} (M \bar{X}\, Y) f\, d\alpha - \int_{R_n} \bar{X} (M\, Y) f\, d\alpha - \int_{R^n} b^{\mu\nu} \frac{\partial \bar{X}\, \partial Y}{\partial \alpha^\mu\, \partial \alpha^\nu} f\, d\alpha. \tag{44}$$

Hence

$$M^* Y = -M\, Y + f^{-1} \frac{\partial}{\partial \alpha^\mu} \left[b^{\mu\nu} f \frac{\partial}{\partial \alpha^\nu} Y \right] =$$

$$= \left[-a^\mu + f^{-1} \frac{\partial}{\partial \alpha^\nu} (b^{\mu\nu} f) \right] \frac{\partial Y}{\partial \alpha^\mu} + \frac{1}{2} b^{\mu\nu} \frac{\partial^2 Y}{\partial \alpha^\mu\, \partial \alpha^\nu}. \tag{45}$$

In order to obtain $T\,M\,T$ we consider

$$T\,M\,T\,X(\alpha) = M\,T\,X(T\,\alpha) = a^{\mu}(T\,\alpha)\frac{\partial\,T\,X}{\partial\,\alpha^{\mu}}(T\,\alpha) + \frac{1}{2}b^{\mu\nu}(T\,\alpha)\frac{\partial^{2}\,T\,X}{\partial\,\alpha^{\mu}\,\partial\,\alpha^{\nu}}(T\,\alpha) =$$

$$= a^{\mu'}(T\,\alpha)\,T^{\mu}_{\mu'}\frac{\partial\,X}{\partial\,\alpha^{\mu}}(\alpha) + \frac{1}{2}b^{\mu'\nu'}(T\,\alpha)\,T^{\mu}_{\mu'}\,T^{\nu}_{\nu'}\frac{\partial^{2}\,X}{\partial\,\alpha^{\mu}\,\partial\,\alpha^{\nu}}(\alpha). \quad (46)$$

Equating (45) and (46) we find

$$a^{\mu'}(T\,\alpha)\,T^{\mu}_{\mu'} = -a^{\mu}(\alpha) + f(\alpha)^{-1}\frac{\partial}{\partial\,\alpha^{\nu}}[b^{\mu\nu}(\alpha)\,f(\alpha)], \quad (47)$$

$$b^{\mu'\nu'}(T\,\alpha)\,T^{\mu}_{\mu'}\,T^{\nu}_{\nu'} = b^{\mu\nu}(\alpha). \quad (48)$$

We recall that equation (30) has the form of an incompressibility relation

$$\frac{\partial\,J^{\mu}(\alpha)}{\partial\,\alpha^{\mu}} = 0. \quad (49)$$

The general integral of (49) can be written

$$J^{\mu}(\alpha) = \frac{1}{2}\frac{\partial\,(c^{\mu\nu}(\alpha)\,f(\alpha))}{\partial\,\alpha^{\nu}} \quad (50)$$

where

$$c^{\mu\nu}(\alpha) = -c^{\nu\mu}(\alpha)\,{}^{1}. \quad (51)$$

Hence we find the following representation for $a^{\mu}(\alpha)$

$$f(\alpha)\,a^{\mu}(\alpha) = \frac{\partial}{\partial\,\alpha^{\nu}}[L^{\mu\nu}(\alpha)\,f(\alpha)] \quad (52)$$

where

$$L^{\mu\nu}(\alpha) = \tfrac{1}{2}[b^{\mu\nu}(\alpha) + c^{\mu\nu}(\alpha)]. \quad (53)$$

From (52) we obtain easily the following representations of M and M^*, (45):

$$M\,X = f^{-1}\frac{\partial}{\partial\,\alpha^{\nu}}\left[f\,L^{\mu\nu}\frac{\partial\,X}{\partial\,\alpha^{\mu}}\right], \quad (54)$$

$$M^*X = f^{-1}\frac{\partial}{\partial\,\alpha^{\nu}}\left[f\,L^{\nu\mu}\frac{\partial\,X}{\partial\,\alpha^{\mu}}\right]. \quad (55)$$

We propose that it is possible to choose $c^{\mu\nu}(\alpha)$ so that $L^{\mu\nu}(\alpha)$ satisfies the symmetry relation (7). As is seen from (48) the symmetry relation is valid for the symmetric part of $L^{\mu\nu}(\alpha)$, i.e. $\frac{1}{2}\,b^{\mu\nu}(\alpha)$. It is therefore sufficient to show that $c^{\mu\nu}(\alpha)$ can be chosen so that it satisfies (7). Assume that $c_1{}^{\mu\nu}(\alpha)$ satisfies (50) and define $c^{\mu\nu}(\alpha)$ by

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[1] This is wellknown i the 3-dimensional case: If $\nabla\cdot\vec{J} = 0$ we can write $\vec{J} = \nabla\times\vec{A}$.

$$c^{\mu\nu}(\alpha) = \tfrac{1}{2}\left[c_1^{\mu\nu}(\alpha) + c_1^{\nu'\mu'}(T\alpha)\, T^{\mu}_{\mu'} T^{\nu}_{\nu'}\right]. \tag{56}$$

It is evident that $c^{\mu\nu}(\alpha)$ defined by (56) satisfies the symmetry relation (7) so that we have only to prove that it satisfies (50). We find, using (47), after an elementary calculation

$$\frac{1}{2}\frac{\partial}{\partial\alpha^{\nu}}\left[f(\alpha)\, c_1^{\nu'\mu'}(T\alpha)\, T^{\mu}_{\mu'} T^{\nu}_{\nu'}\right] = \frac{1}{2}\frac{\partial}{\partial\alpha^{\nu}}\left[f(\alpha)\, c^{\mu\nu}(\alpha)\right]. \tag{57}$$

and this completes the proof.

5. The derivation of the reciprocal relations (7) for the non linear system (6) has been based on the time reversal invariance of the mechanical equations of motion and on the assumptions about the behaviour of the transition probability distribution (11) for *macroscopically small* time differences expressed by Kolmogorov's condition. It should be noticed that we have made no assumptions about the behaviour of the transition probability distribution for large time differences. In particular we have *not* assumed that the transition probability distribution corresponds to a Markov process. It is evident that the assumptions underlying Kolmogorov's second condition are compatible with statistical mechanics only on a sufficiently coarse grained time scale. This is evidently the same assumption as used in the linear theory (see in particular [Smoluchowski, 1916]). The conditions of Kolmogorov determine the behaviour of the transition probability distribution for macroscopically small time differences only, in fact they determine only the derivative with respect to time at the origin of time, whereas all further properties of the transition probability distribution remain unspecified and are irrelevant to our discussion.

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